FIRST ANNUAL PROGRESS REPORT

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"Transport Limitations in Selective Diamond Deposition"

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ACCOMPLISHMENTS THIS PERIOD:

In the past year, we have made progress toward understanding of the mass transport limitations in diamond deposition by using selective deposition to control diamond nucleation. To start with, our deposition process was improved to give consistent, reasonable selectivity (see Figure 1). Background nucleation densities are typically less than 10^5 cm^{-2} while seeded areas generally have a nucleation density of at least 10^7 cm^{-2}.

A new photolithographic mask was designed and implemented at MIT's Lincoln Laboratories to take advantage of their 0.6 μm linewidth process so that we may deposit lines or dots of diamond consisting of individual crystals (see Figures 2a and 2b). A sample with the regular rectangular array of diamond crystals has been sent off to SI Diamond for testing in potential cold cathode applications (Figure 2b).

Additional features were added to the mask to probe for growth variations in the 1-150 μm range (see Figure 3). Under controlled conditions, deposition on a selectively nucleated wafer showed no significant variations in growth rate as a function of feature geometry and spacing, implying that the relevant mass transport length is greater than 300 μm. By modeling this behavior in two dimensions with a finite difference scheme that includes gas phase diffusion from the filament to the substrate surface and a first order surface reaction, we deduced that the selectively deposited diamond features can be treated as contributing to a surface coverage weighted average reactivity versus through a more detailed accounting of the surface geometry. This simplification allows us to model fine scale features (e.g. micron length scales) deposited over a much larger area (e.g. centimeters).

In order to examine mass transport limitations on a larger scale, diamond was selectively deposited on a centimeter scale pattern (see Figure 4). By analyzing the variation in growth rate of diamond crystals along the centerline in the mask pattern, transport effects over millimeter length scales were examined. (Figures 5a and 5b are the results of a typical 2 hour deposition.) Using image analysis software, we digitized these electron micrographs and generated histograms of crystallite size. Typically, a Gaussian distribution of particle sizes is obtained at any one point. A comparison of histograms shows a significant difference in the growth rate of individual particles between the middle and the end of the centerline (see Figure 6).

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This centimeter scale experiment has been modeled by considering the gas phase composition in three dimensions and by using the average surface reactivity concept that resulted from the smaller dimension mask. Figure 7 is a graph of the predicted concentration directly above the substrate surface and is directly proportional to the diamond growth rate for a first order reaction. Figure 8 displays the predicted growth rate along the centerline as a function of the dimensionless number $(\frac{kL}{d})$, where k is the first order surface reaction coefficient, L is the characteristic pattern length and d is the gas phase diffusion coefficient. For a value of $\frac{kL}{d} \approx 8$, the growth rate variation shown in Figure 6 is correctly predicted by the model. By matching both the absolute value and the variation in the growth rate given by the model to the experimental results, we will be able to calculate a value for k and thereby infer the identity of the relevant growth precursor as well as quantify the extent to which mass transport effects limit growth.

GOALS AND PLANS FOR NEXT PERIOD:

Over the next year, we plan to continue our experiments in the hot-filament CVD system at MIT. Varying the temperature of the substrate should have an exponential effect on the growth rate as well as a predictable effect on the growth rate variation. In addition we plan to examine the effects of varying the gas phase carbon concentration and the pressure in the reactor on the growth rate of diamond on our selectively deposited substrates. For comparison to hot-filament CVD, selective depositions will be done in a microwave system in collaboration with ASTEX. We plan on doing a baseline deposition as well as a set of substrate temperature variation experiments. The microwave reactor's advantage is that it should yield a more uniform generation of gaseous deposition precursors as well as inform us if the chemistry of gas phase activation needs to be considered when modeling selective depositions. The modeling work will also be extended to describe the microwave CVD reactor geometry. In addition, we will progressively eliminate assumptions used in our current model in order to determine the complexity needed to interpret the experimental results. If successful, these experiments will give us a better fundamental understanding of how mass transport affects growth and help us to maximize the growth rate and uniformity of selectively deposited diamond films.

PUBLICATIONS AND PRESENTATIONS

As a result of this AASERT award:

Michael C. Kwan and Karen K. Gleason, "Surface Diffusion Effects in the Nucleation and Growth of Chemical Vapor Deposited Diamond Films", presented at the National Meeting of the American Institute of Chemical Engineers, San Francisco, November, 1994.

Resulting from the recently expired parent grant:

Karen K. Gleason, "Application of ^{1}H, ^{13}C and ^{19}F to Diamond Thin Films", presented at the Gordon Conference on Diamond, New Hampshire, June 1994.

K. M. McNamara, B.E. Scruggs and K.K. Gleason, "Influence of hydrogenated defects and voids on the thermal conductivity of polycrystalline diamond", J. Appl. Phys. **77**, 1459 (1995).

K.M. McNamara, B.E. Williams, K.K. Gleason and B.E. Scruggs, "Identification of Defects and Impurities in Chemical Vapor Deposited Diamond through Infrared Spectroscopy", J. Appl. Phys. **76**, 2466 (1994).

K.M. McNamara, B.E. Scruggs, and K.K. Gleason, "The Effect of Impurities on the IR Absorption of Chemically Vapor Deposited Diamond", Thin Solid Films **253**, 157 (1994).

INVITED REVIEWS

K.K. Gleason, "Diamond Thin Films" for the "Encyclopedia of Nuclear Magnetic Resonance" edited by D.M. Grant and R.K. Harris (Wiley, to be published 1995).

Karen M. Rutledge and Karen K. Gleason, "Characterization Methods" for the "Industrial Handbook of Diamond and Diamond Films" edited by K. Bigelow (Marcel Dekker, to be published 1995).

AWARDS

Karen K. Gleason was elected vice-chair of the 1996 Gordon conference on diamond synthesis.

Karen K. Gleason was promoted to associate professor with tenure at MIT.
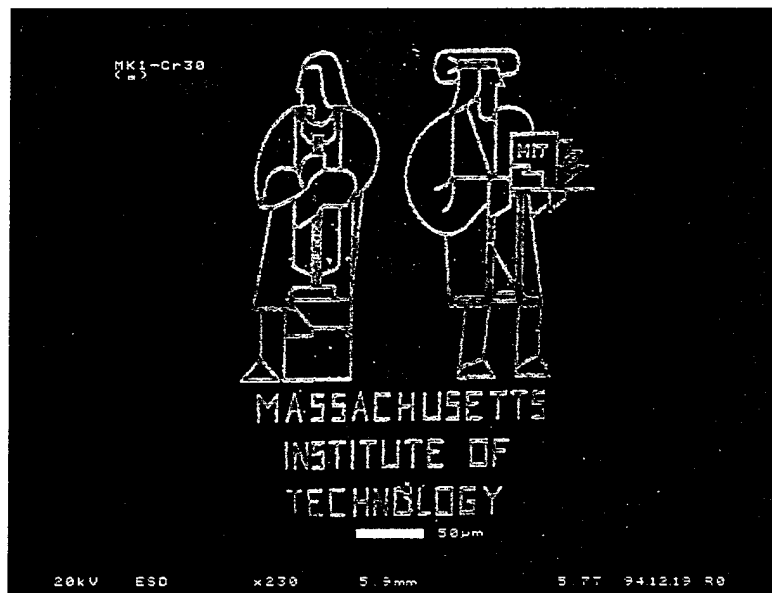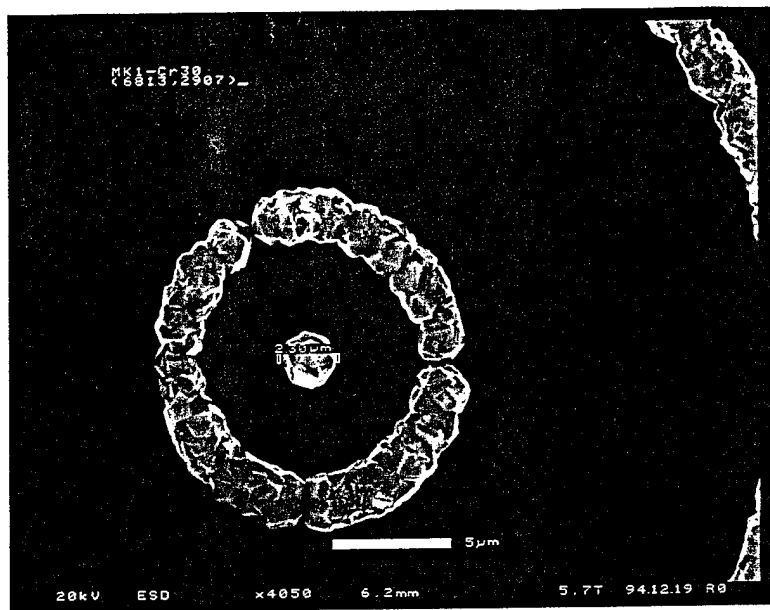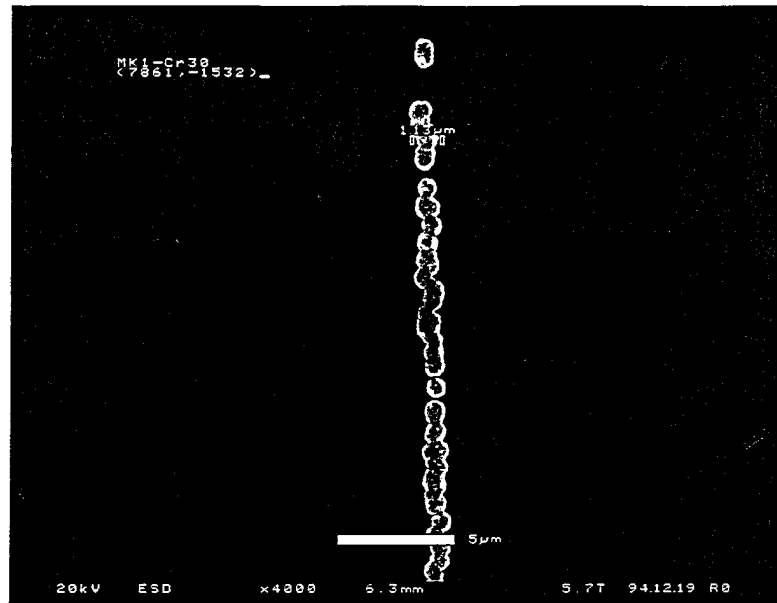
Figure 1: examples of selectively deposited diamond

Figure 2a: micrograph of a selectively deposited "line" of
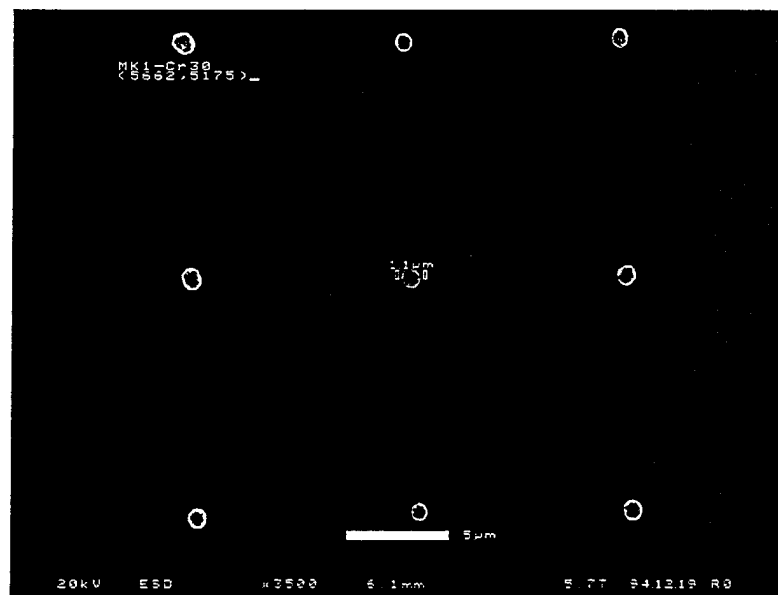diamond using the 0.6 μm linewidth process

Figure 2a: micrograph of a selectively deposited diamond
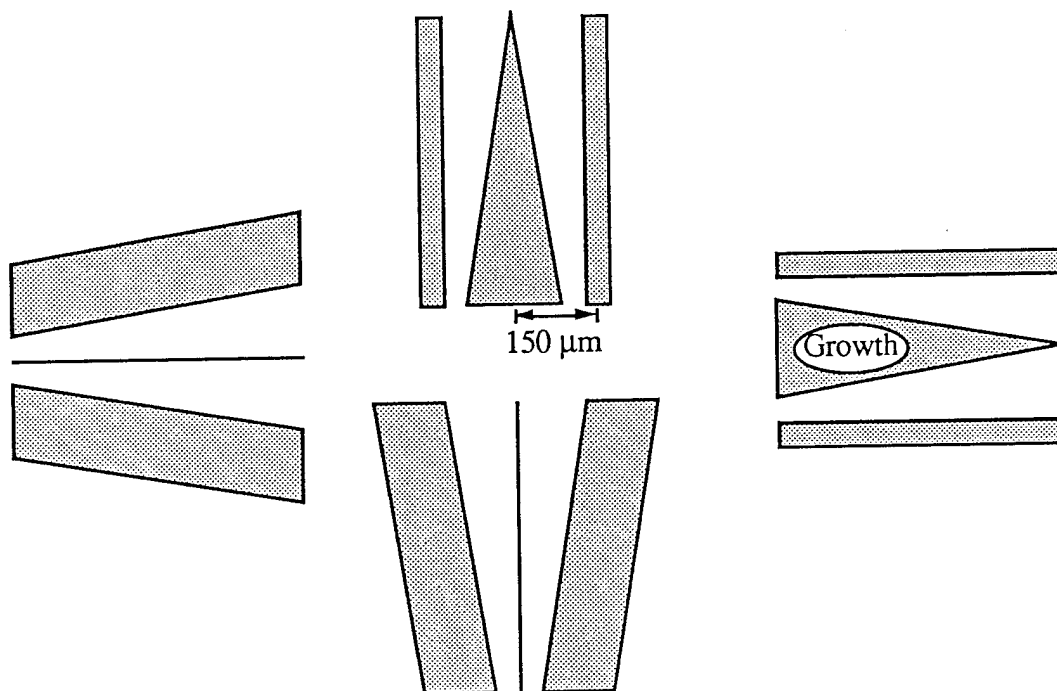"dots" using the 0.6 μm linewidth process

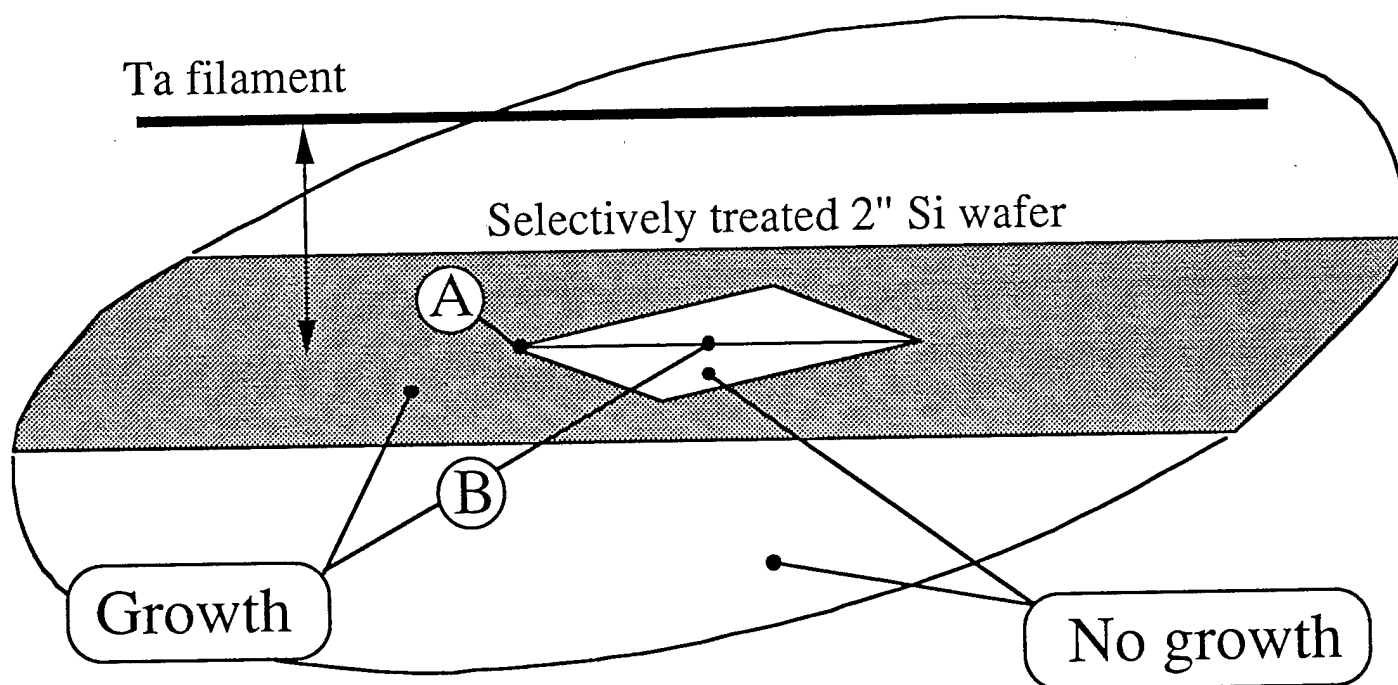Figure 3: Selective deposition patterns added to mask
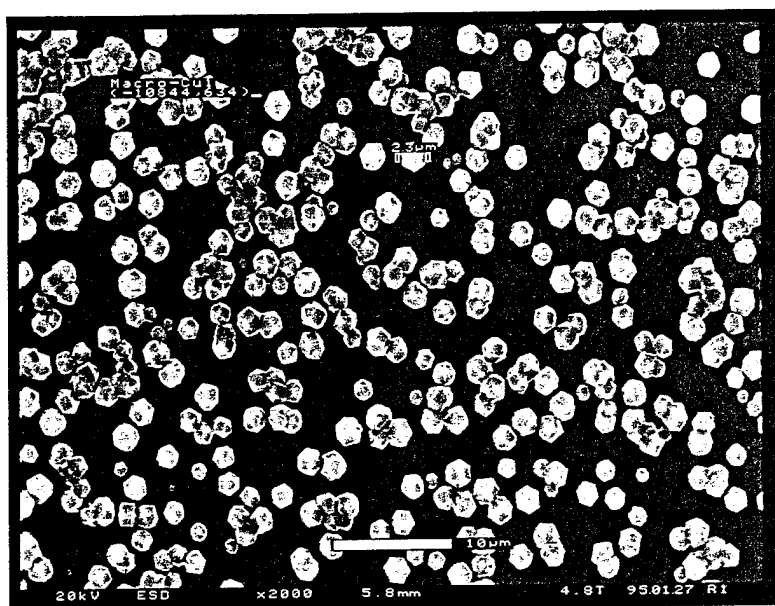

Figure 4: Selectively deposited pattern

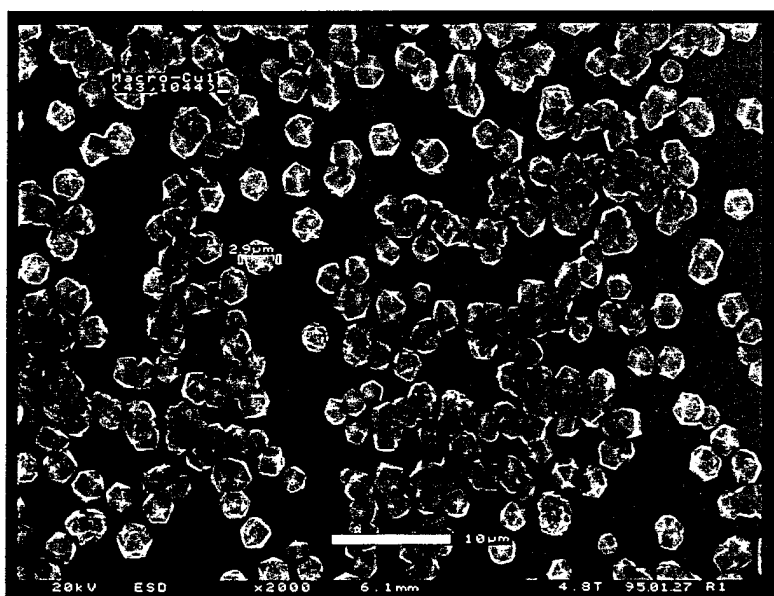Figure 5a: micrograph of a typical 2 hr deposition (taken at point A in Fig. 4)

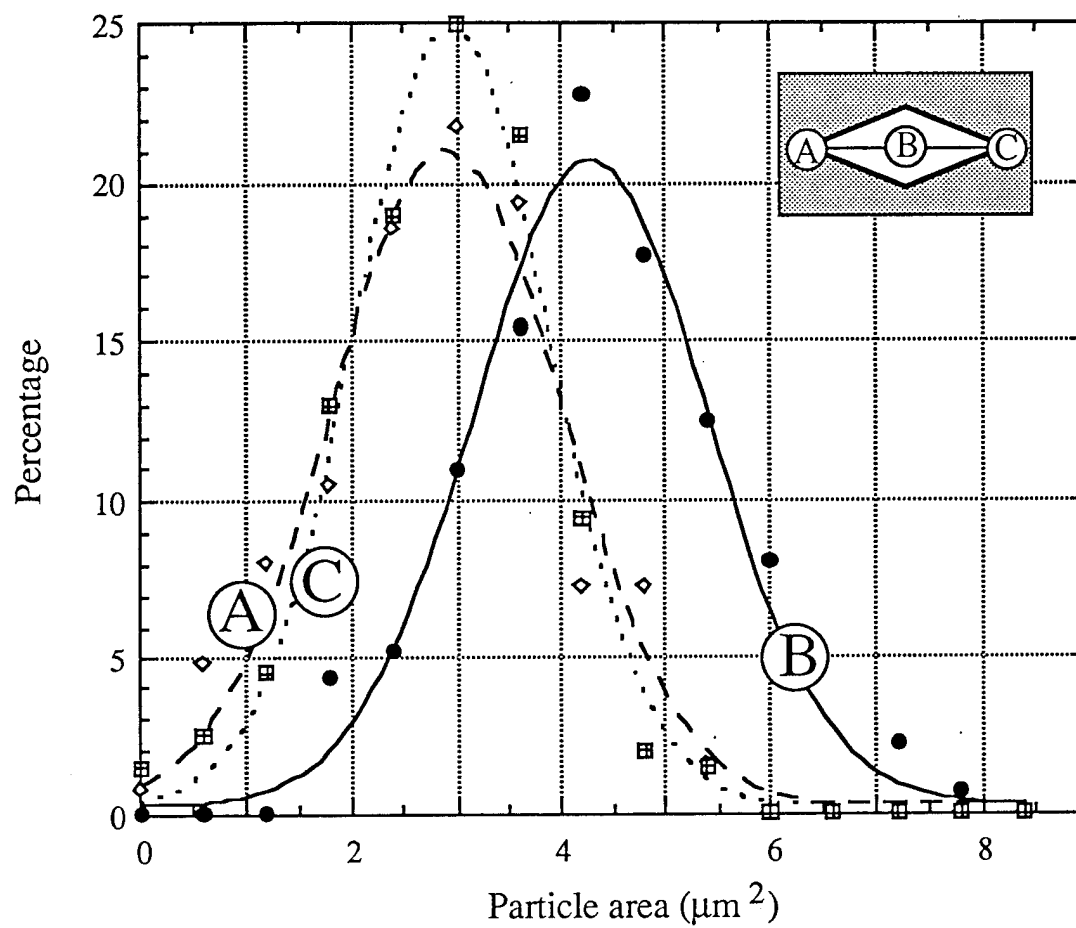Figure 5b: micrograph of a typical 2 hr deposition (taken at point B in Fig. 4)

Figure 6: experimentally measured particle size distributions
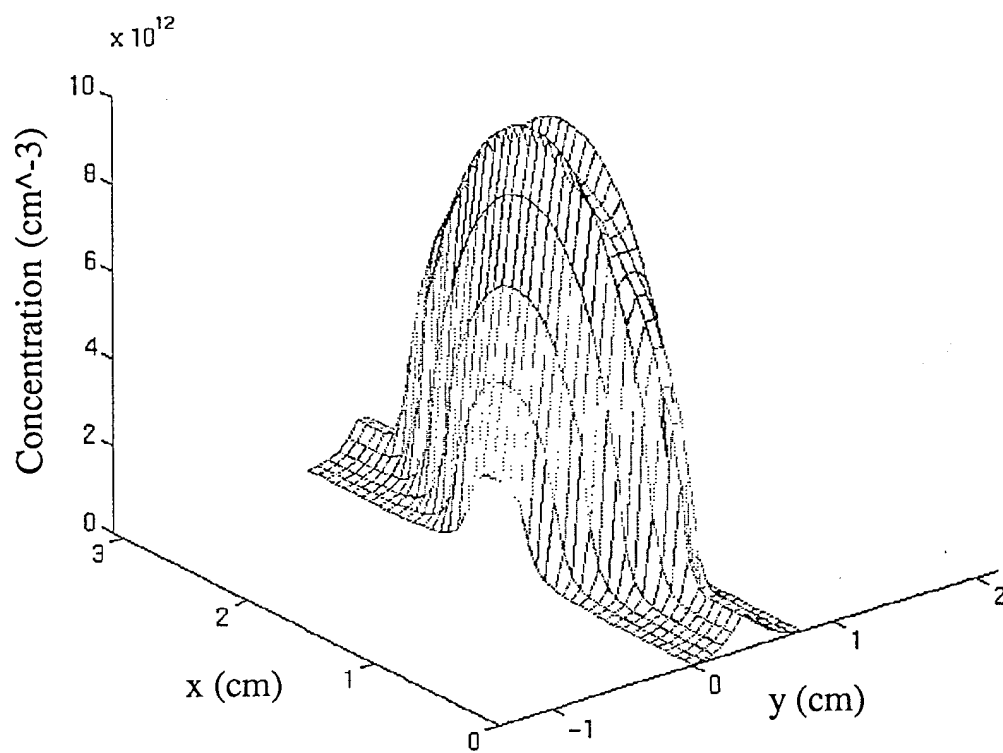[distributions A & B correspond to points A & B in Fig. 4]

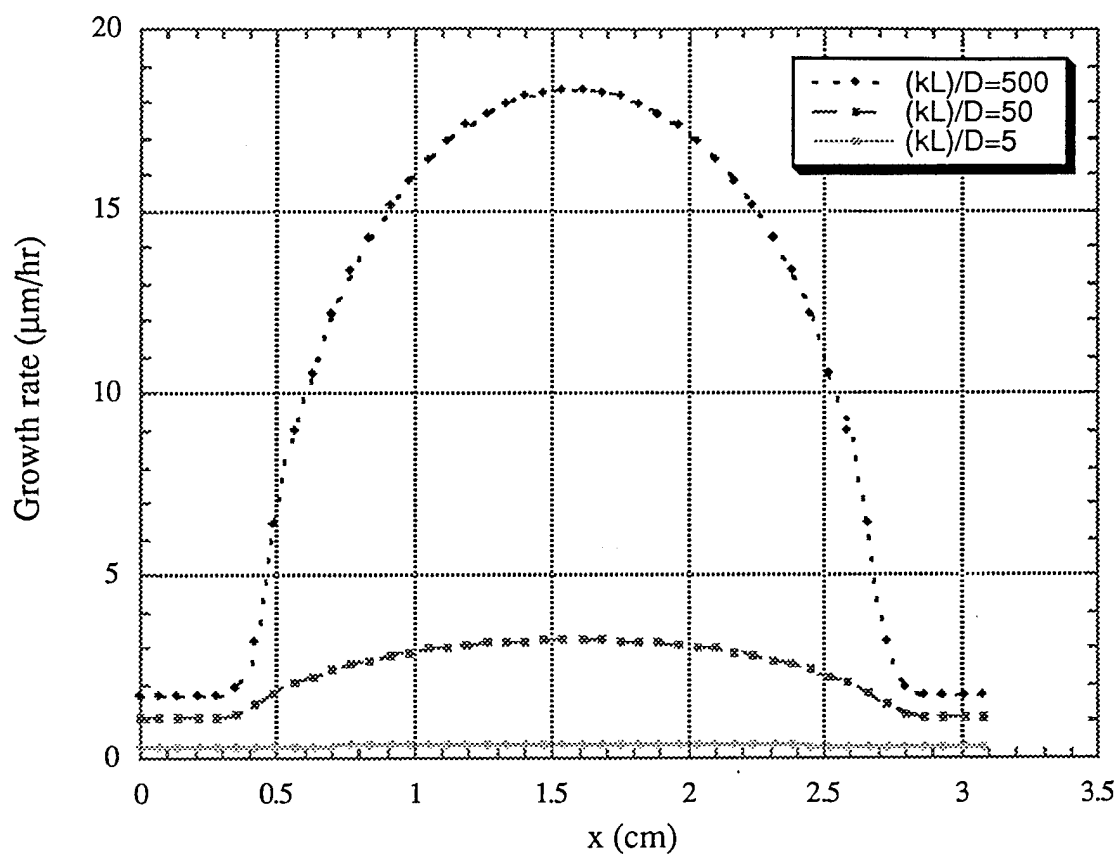Figure 7: Predicted concentration directly above substrate surface

Figure 8: Predicted growth rate variation along centerline

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13. ABSTRACT (Maximum 200 words)

A high-selectivity diamond deposition process has been developed for feature sizes ranging from 0.6 μm to 2 cm. Variations in diamond growth rate as a result of this patterning have been observed and modeled by a finite difference method. This work provides a critical test of the interplay between surface kinetics and mass transport effects on the chemical vapor deposition process. The control of crystallite spacing may prove useful in fabrication of devices for cold-cathode emission and in growing contiguous polycrystalline films with well-defined grain structure.

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